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Effect of raw material and Kraft Pulping Conditions on Characteristics of Dissolved Lignin

Degree Project in Pulp technology KF274X

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Abstract

Lignin is one of the main components in wood and during the chemical pulping processes it is degraded and dissolved into the cooking liquor. The current challenge is to meet the need for energy and raw materials, and reform to a more environmentally sustainable society, so there is a great interest in using kraft lignin as a raw material for energy, materials and as source of chemicals.) To meet this goal, it is essential to obtain kraft lignin with desirable properties. The overall goal of this master thesis project was to understand the relationship between kraft process conditions and the structure and properties of the dissolved lignin.

Wood chips of pine, spruce and eucalyptus were pulped with the kraft process at constant temperature and similar alkali charge and sulphidity to different cooking times. From the collected black liquor, the dissolved kraft lignin was precipitated by acidification with sulphuric acid. It was observed that longer cooking time yields more precipitated material, where pine gave the highest yield. There was a significant difference in colour of the precipitated between eucalyptus and the softwood samples.

Some the characteristic properties of the collected samples were investigated. Results from the Klason lignin and ionic chromatography showed variation in lignin and carbohydrate composition depending on raw material and cooking time. This was also indicated by results lignin carbohydrate ratio from analytical pyrolysis. However, the analytical pyrolysis data showed that the relative composition of lignin and carbohydrates was similar independent on pulping time and raw material. The sulphur content was higher for eucalyptus lignin compared to the softwood lignin. Pine lignin with the longest pulping time had the highest total phenolic content. Spruce lignin with the longest cooking time had the highest glass transition temperature.

Sammanfattning

Lignin är en av de största byggstenarna i träd och andra växtmaterial, både till storlek och mängd. Under kemiska massaframställningsprocesser, som sulfatprocessen, bryts strukturen ned och lignin löses ut i kokvätskan. Ligninets värmevärde tas till vara, genom att det förbränns i sodapannan. Med den utmaning som dagens samhälle står inför, där fossila råvaror ska ersättas med förnyelsebara, finns ett allt större intresse att se vilka andra användningsområden som kan finnas för lignin, som grön råvara för energi, material och kemikalier. Det krävs därför kunskap om hur lignin med lämpliga egenskaper ska kunna utvinnas. Målet med detta examensarbete var att undersöka hur vedråvara och koktid under sulftakoket påverkar egenskaper hos det utlösta ligninet.

I denna studie kokades vedflis av tall, gran och eukalyptus enligt sulfatprocessen och det utlösta ligninet analyserades efter tre olika koktider. Längre koktid ledde till mer utfällt material. Det var en tydlig skillnad i färg mellan lignin från eukalyptus och de från barrveden, gran och tall Eukalyptusligninet var mörkare med en tydlig grönaktig färgskiftning. Längre koktid medförde även ett mer lättfiltrerbart lignin.

Mängden lignin, bestämt som mängd Klason lignin efter sur hydrolys, var högre i utfällningen efter kok av eukalyptus jämfört med efter kok av barrved. Resultaten från den analytiska pyrolysen visar däremot på rakt motsatt förhållande. Enligt den analytiska pyrolysen är det något mindre mängd lignin i utfällningen efter eukalyptuskok. Orsaken kan vara att vid kvantitativ bestämning av lignin som Klason lignin, kommer det oorganiska materialet att fällas ut tillsammans med ligninet, varvid mängden Klason lignin även inbegriper askmängden. Mängden lignin som lösts ut under koket ökar med ökad koktid, men andelen lignin i det utfällda materialet ändras inte med koktiden. Svavelhalten var högre för (utlöst) eukalyptuslignin än för granlignin och talllignin. Talllignin med den längsta koktiden hade den högsta totala halten fenol. Gran lignin med den längsta koktiden hade det högsta värdet på glastransitionstemperaturen.

Innehåll

1. Introduction

Lignin is one of the main biopolymers in plants which during the kraft pulping process are dissolved into the cooking liquor. During the recovery of cooking chemicals in the kraft process lignin is mostly burned for energy in the recovery boiler. The recovery boiler is usually working at maximum capacity, which makes it the bottleneck of the process and thereby limits the production capacity since it is a large capital investment for capacity increase. In the biorefinery concept lignin is of great interest as a source for bioenergy and biofuel, i.e. used as the pulp mill energy generation and/or replacing the use of fossil fuel in the lime kilns (high energy demanding processes in which the white liquor is regenerated). Moreover, kraft lignin is increasingly interesting as a source of material for carbon fibres, plastics and source of phenolic monomers. In a novel biorefinery concept it is of great importance to know if the effect of raw material and process conditions which yields desirable characteristics of obtained kraft lignin to further development of usable product streams. In this master thesis, wood chips of eucalyptus, pine and spruce were subjected to kraft pulping to three different cooking times and lignin precipitated from the spent liquors.

The aim of this study was to investigate and compare the impact of raw material (eucalyptus, pine, spruce) and kraft cooking conditions on the composition and some physico-chemical properties of lignin isolated from the black liquor.

2. Background

2.1 Lignin in wood

Lignin is one of the most abundant biopolymers and not restricted to woody plants but occurs in all vascular plants. The biological function of lignin is to give stiffness to the cell walls, glue the cells together in woody tissues, make the cell wall hydrophobic, and protect the tree from microbial degradation and a stabilizer to UV radiation action (Henriksson 2010). Table 1 below shows the relative amount of biopolymers in wood species relevant to this project.

Table 1 - Composition of biopolymers in pine, spruce and eucalyptus (Sjöström 1993)

	Pine (%)	**Spruce (%)**	**Eucalyptus (%)**
Cellulose	39	41	45-51
Xylan	8	8	11-20
Glucomannan	17	18	2-4
Lignin	27	27	22-24
Extractives	4	2	2-4

Lignin is not uniformly distributed within the wood and also the content as well as the composition will vary considerably depending on type of wood and growing conditions. Also the amount and composition of lignin varies among wood cell types, individual cell wall layers and middle lamella. The wood cell contains several layers where lignin encrusts the cellulose in the cell wall layers and acts as an intercellular binder in the middle lamella between wood cells. The cell wall layers are divided into the primary wall (P) and secondary wall. The lignin concentration is higher in the middle lamella (about 55% of the ML material) and in the cell corners (90%) than in the secondary wall, but since the secondary wall occupies a larger portion of the fibre cell wall, it will have the highest amount of lignin (Daniel 2010).

The structure and properties of lignin is of great interest in pulping and bleaching, but also lately in the concept of a biorefinery as there is an increased need to find new, more neutral carbon sources of non-fossil origin for materials production. The structure is versatile but can be classified in two broad categories; hardwood lignin and softwood lignin, depending on the species of tree and on the monolignols the lignin is polymerized from. The three main monolignols are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Figure 1 shows the structure of the monolignols, and table 2 shows the composition of monolignols in softwood and hardwood (Henriksson 2010).

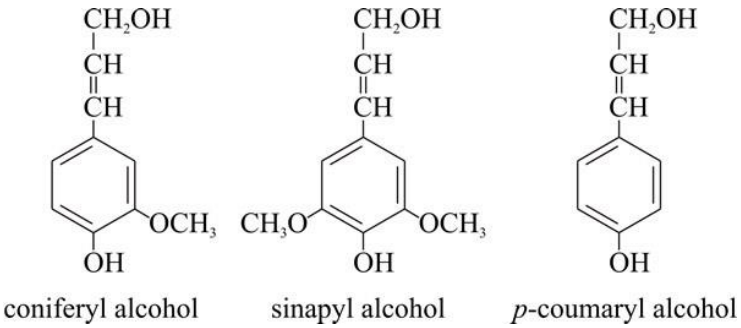

Figure 1 - Chemical structure of the monolignols

Table 2 - Composition of monolignols in in softwood and hardwood lignin

	Coniferyl alcohol (%)	**Sinapyl alcohol (%)**
Spruce/Pine	>95	None or Trace
Eucalyptus	25 - 50	46 – 75

The main chemical bond that builds the lignin network structure is the phenolic and non-phenolic ether, covalent carbon-carbon bonds, also called condensed bonds, and lignin carbohydrate linkages. The lignin network consists mostly of aromatic phenols and the condensed bonds occur in condensed clusters with no more than four units. The most important bond is the β-O-4 bond between monolignols which according to table 3 below is the most common bond in lignin albeit at different frequency depending on type; softwood or hardwood (Henriksson 2010).

Table 3 - Composition of the most common bonds in softwood and hardwood lignin (Santos et al. 2013)

Linkage type	**Dimer structure**	**Linkages in Softwood (%)**	**Linkages in Hardwood (%)**
β-O-4´	Arylglyceryl β-aryl ether	45-50	60
5-5’	Biphenyl and Dibenzodioxocin	18-25	20-25
β-5’	Phenylcoumaran	9-12	6
β-1’	1,2-Diaryl propane	7-10	7
α-O-4’	Phenylpropane α-aryl ether	6-8	7
4-O-5’	Diaryl ether	4-8	7
β-β’	β-β- linked structures	3	3

The composition of monolignol decides the types of bond that builds up the lignin network. Hardwood lignin is mainly built up of coniferyl and sinapyl alcohol which gives a more heterogeneous structure than softwood lignin but contains more β-O-4 linkages and less condensed bonds. Whereas in the case of softwood lignin the structure is built up mostly by coniferyl alcohol that gives a more homogeneous structure compared to hardwood lignin but will contain more condensed bonds. The lignin network structure will vary little depending on species for softwood but for hardwood it's another matter. There is increasing evidence from recent studies that the hardwood lignin network structure will vary considerably in different species and also among species of the same genus and even among clones. Also, in case of hardwood the lignin structure will also vary in the wood cell structure, the lignin structure will have a more typical hardwood structure in the secondary cell wall layer while the middle lamella lignin is more that of softwood lignin and this is of great importance in delignification chemistry in kraft cooking. In lignin chemistry the way to measure and not the difference in hardwood lignin and softwood lignin is the variation of the S/G ratio (syrangyl/ guaiacyl ratio corresponding to amount of syringyl and guaiacyl structural units). Syringyl units are the structural unit of sinapyl alcohol and with the most β-O-4 bonds, while guaiacyl is the structural unit of coniferyl alcohol with more condensed carbon carbon bonds. Thereby there will be different S/G ration for hardwood and softwood in the middle lamella and secondary cell wall Henriksson 2010; Santos et al. 2013).

The complexity of the network structure is further added by an abundance of functional groups present in the lignin macromolecule. The most common is methoxyl groups, about 92-96 per 100 phenyl propane units (PPUs), followed by free phenolic hydroxyl groups, 15 – 30 per 100 PPUs, benzyl alcohols, 15 – 20 per 100 PPUs, carbonyls, 10 – 15 per PPUs, and a few terminal aldehyde groups. The aromatic rings and hydroxyl groups in lignin allows formation of non-covalent dipole-aromatic interaction and hydrogen bonds to all major polysaccharides; hemicelluloses, cellulose and pectins. (Henriksson 2010). But lignin will also be covalently bonded and even crosslinked with the carbohydrates in so-called called Lignin Carbohydrate Complex (LCC) (Lawoko et al. 2005; Santos et al. 2013). The LCC structures is known to be responsible for the poor delignification in the residual phase in kraft cooking (Santos et al. 2013).

2.2 Dissolution of lignin during kraft pulping

2.2.1 The kraft pulping process

Kraft pulping is currently the dominant chemical process used to produce pulp in the world. Invented by Carl F. Dahl year 1879 it gave stronger pulps, due to higher fibre strength, compared to the sulphite process, which was the main chemical process at that time. However, it was not economically feasible until the early 1930s when G.H Tomlinson invented the recovery boiler to recover the cooking chemicals and thereby closing the cooking process with regards to the inorganic chemicals, as well as introducing chlorine dioxide for bleaching since the kraft pulp was more difficult to bleach than sulphite pulp (Sjöström 1993). There are also disadvantages; the major one being the loss of pulp yield, especially compared to mechanical pulping, due to carbohydrate instability and degradation in the elevated temperature and alkaline environment during cooking. The main objective of the process is to liberate the wood fibres from the wood matrix to obtain pulp. This is achieved by preferably removing lignin, while preserving the molecular weight of the carbohydrates as much as possible. Typical outline of the process is wood handling (which includes debarking, chipping, and screening), cooking in digester (referred as kraft cooking), and oxygen delignification, washing of pulp, multistage bleaching and drying of pulp or paper/board making.

In the pulp mill, wood chips are feed in to a batch or continuous digester together with the cooking liquor, the white liquor, containing sodium hydroxide (NaOH) and sodium sulphide (NaSH). The first step is an impregnation step where the white liquor is transported to through the surface of the wood chip followed by penetration and diffusion into the interior of the wood chip. The cooking temperature is normally 135-160°C and as the wood chips are heated the delignification reactions starts, in which the lignin structure is

broken down and lignin and other degradation products diffuses to the exterior where lignin is solubilized into the alkaline solution. The charge of hydroxide ions, hydrogen sulphide ions, sodium ions and the cooking temperature and cooking time is the parameters that decide the cooking conditions and the properties of the final pulp produced in the process. Cooking time and temperature are closely related since a higher temperature makes chemical pulping reactions proceed faster and thereby a shorter cooking time is needed. By combining the simultaneous influences of cooking time and temperature on the rate of delignification the concept of H-factor as a kinetic model is used.

The rate determining step for pulping is the liquor diffusion into the wood structure since the delignification reactions is much faster. Kraft pulping occurs in three kinetic phases; the initial phase, bulk phase and residual phase, see figure 2. The initial phase is mainly extraction of lignin and carbohydrates, removing approximately 20 % of each. Then in the bulk delignification phase the kinetics changes dramatically and a selective lignin degradation and dissolution takes place until about 90 % of the original amount of lignin has been dissolved. At the transition point between the bulk delignification phase and residual delignification phase, the cook has to be terminated since in the residual delignification phase the final portion of the lignin is predominantly unreactive lignin formed by condensation reactions during the cook and LCC structures that can only be removed with great difficulty and with great carbohydrate loss (Gellerstedt. 2010a, Santos et al. 2013; Chakar and Ragauskas 2004).

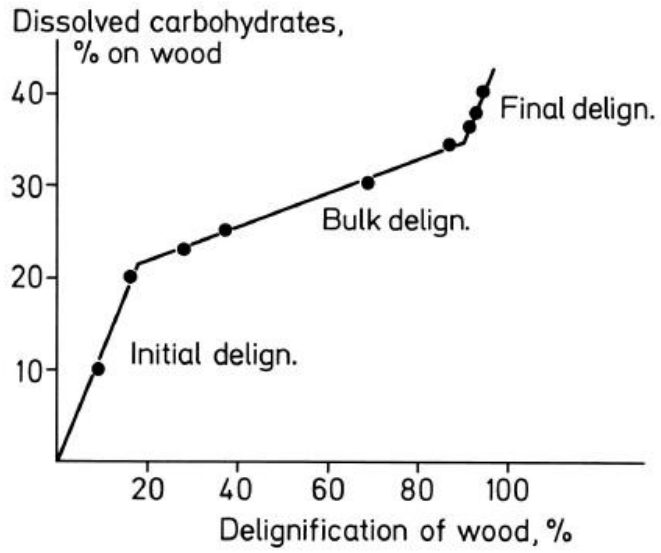

Figure 2 - Selectivity in the dissolution of lignin and carbohydrates on kraft pulping of softwood (Gellerstedt. 2010)

2.2.2 Chemical reactions during kraft pulping

Lignin degradation proceeds through the cleavage of linkages between phenyl propane units thereby fragmenting the lignin network structure and with a constant generation of free hydroxyl groups which increases the hydrophilicity of the lignin fragments. Chemical reactions in the kraft process can be divided into two groups; those that involve lignin and those that involve carbohydrates. The lignin reactions can be classified under two different headings: degradation and counteracting reactions. The major fragmentation reaction in kraft pulping is the cleavage of the phenolic β-O-4' structures by a nucleophilic attack of the hydrogen sulphide ion on a quinone methide. Structural differences in lignin, between hardwood and softwood as well as the difference in type of hemicellulose, affect greatly the pulping conditions and delignification and carbohydrate reactions during cooking. Hardwood with its lower lignin content, less condensed lignin structure and with more β-O-4' bonds will be cleaved faster compared to softwood.

Figure 3 depicts the two main β-O-4' delignification reaction in which hydrogen or RO^- group are lost thus forming an intermediate quinone methide structure. In the first reaction, non-phenolic β-O-4' structures reacts due to the high pH and a nucleophilic attack occurs giving an epoxide which in turn is not stable and reacts further with nucleophiles present. In the second reaction, which is the most efficient, the quinone methide is formed from a phenolic structure to which hydrogen sulphide is added to give an episulphide. In subsequent reaction steps the sulphur is lost and the lignin structure is converted in part to a coniferyl alcohol which is in turn degraded due to the high temperature. Each cleavage of β-O-4' during kraft pulping gives rise to a new aromatic end group with a free phenolic hydroxide group which is ionized in the alkaline pulping liquor and thus promotes the solubility of the lignin fragment.

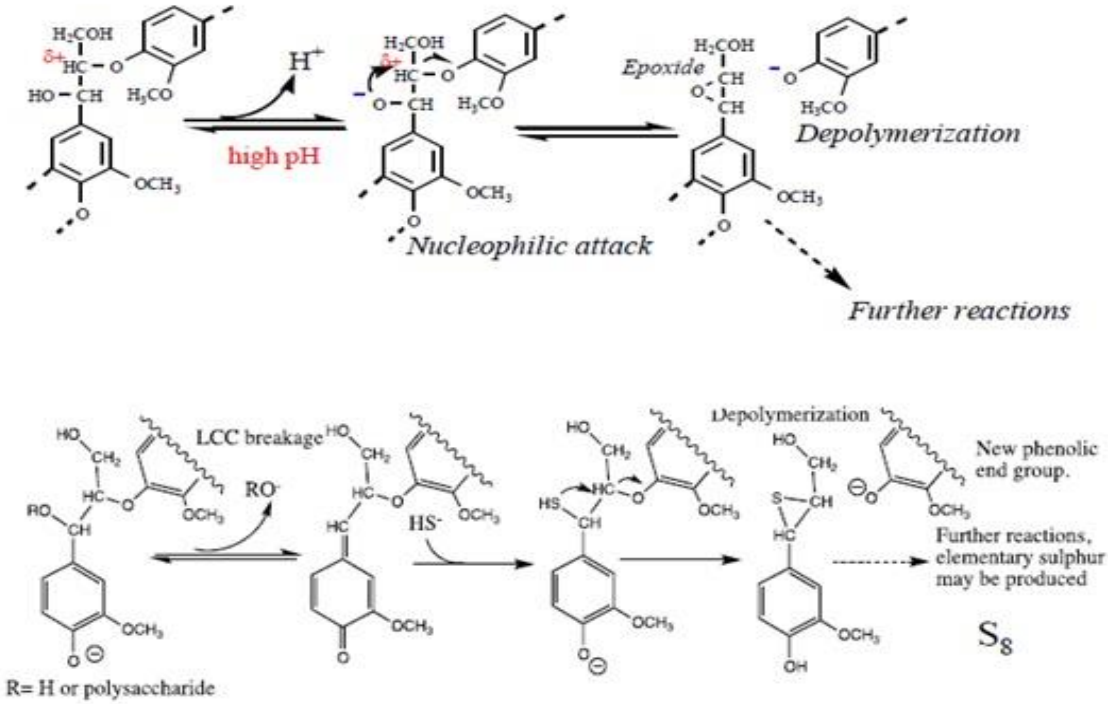

Figure 3 - Two main β-O-4' delignification reactions during kraft pulping (Gellerstedt. 2010a)

The only lignin structure that is totally degraded during kraft pulping is the dinezodioxocin which is one of the most important nodes in the lignin network, see figure 4.

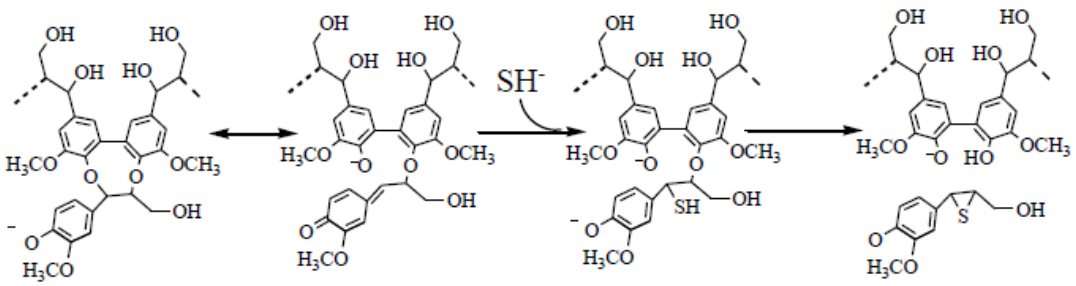

Figure 4 - Degradtion reaction of dibenzodioxocin (Gellerstedt. 2010a)

Despite the efficiency of the β-O-4' cleavage there are some competing reactions which all start at the quinone methide intermediate. The competing reactions include elimination, reduction and condensation reactions as well as formation of bad smelling compounds, such as methyl mercaptan and dimethyl sulphide. (Gellerstedt. 2010a) Condensation reactions involve radical coupling. Radicals are created on the lignin structure from reactions with elementary sulphur. The condensation reactions are more common among glucomannan bound lignin which has the slowest degradable LCC. Almost all residue lignin is LCC structures has different degradation rate depending on bound polysaccharide (Lawoko et al. 2005; Santos et al. 2013).

The main dead-end reaction is the counteraction reaction which leads to the formation of enol ether which is an unreactive structure and these reactions become more common when the sulphide concentration is low (Gellerstedt. 2010a, Santos et al. 2013 and Chakar and Ragauskas 2004).

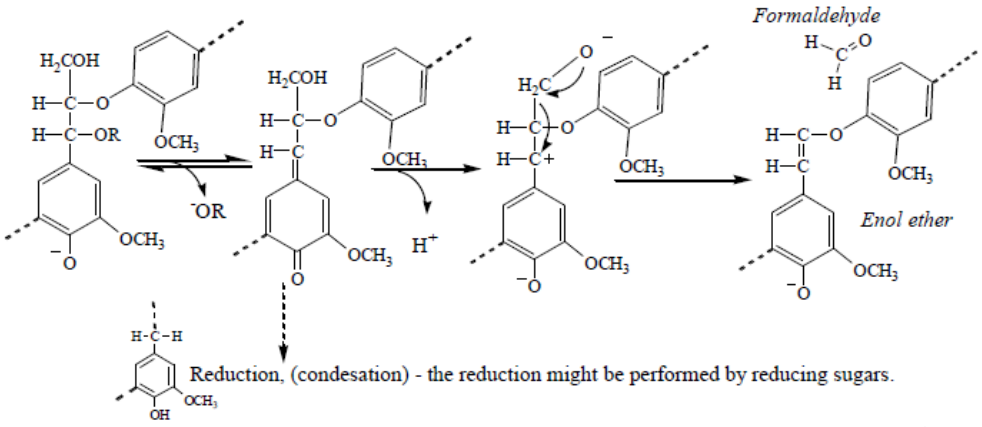

Figure 5 - Formation reaction of enol ether (Gellerstedt. 2010a)

Other lignin reactions are for example the formation of stillbenes form lignin reactions in the β-5' and β-1' structures, but these do not contribute to the delignification but are included in the residual lignin structure in the pulp and is important in bleaching chemistry (Gellerstedt. 2010a, Santos et al. 2013 and Chakar and Ragauskas 2004).

Carbohydrate reactions involve alkaline hydrolysis and peeling both unfavourable and are responsible of the predominant loss of carbohydrates. This is due to the fact that most of the hemicelluloses is degraded and dissolved into the pulping liquor. Thereby is important to consider these reactions to understand the very complex composition of black liquor from which lignin is precipitated. Degradation of hemicelluloses proceeds by two different reactions; the peeling reaction where the polysaccharide units are cut off one by one, and the alkaline hydrolysis where the polysaccharide chain is cut randomly. Reactive glucomannan is easily degraded into smaller molecules, whereas xylan is the exception. Xylan is the predominant hemicellulose in hardwood and the presence of substituent unit as a side chain allows it to act as a leaving group in the peeling reaction and causes the reaction to stop. This stopping reaction allows xylan to maintain most of its molecular mass and is allowed to dissolve into the black liquor. One other of the important carbohydrate reactions during is the formation hexenuronic acid (Hex A) on xylan. Hex A is colourless, but gives problems in bleaching, causing yellowing of bleached pulp and influence the kappa number (a way to measure the residual lignin; see materials and methods). Sulphur undergoes its own sets of reactions which includes creation of elementary sulphur, which can further react with hydrogen sulphide to form polysulphide, which in turn reacts with hydroxide to form thiosulphate or decomposes to hydrogen sulfide. The carbohydrate degradation reactions on cellulose and hemicellulose, sulphur reactions and

degradation reactions of extractives are important to consider because its degradation products contribute to the complex mixture that is the spent cooking liquor (black liquor) from which lignin is precipitated (Gellerstedt. 2010a).

2.2.2 The chemistry of black liquor

The spent cooking liquor, black liquor, is a complex water mixture of organic and inorganic materials, and composition of which depends on cooking conditions applied and species of wood. The organic content originates from dissolved wood and is mainly lignin, hemicelluloses, extractives and degradation products, while the inorganic content originates from the cooking chemicals, mainly sodium ions and trace ions from the incoming wood. The structures of the polymeric and low molecular mass fractions have been comprehensively mapped by Niemelä and Alén 1999. The black liquor is a mixture of monomer and polymer fractions originating from degradation products of lignin, polysaccharides, extractives, proteins and suberin. The polymer fraction of lignin degradation products is kraft lignin and the monomer fraction is phenolic compounds. The polymeric fractions from polysaccharides are hemicelluloses which was not fully degraded during the cook. Monomeric degradation products form the polysaccharides are aliphatic carboxylic acids and different cyclic compounds. Degraded extractives are mostly polyphenols, fatty acids, terpenoids, steroids etc. Table 4 depict the approximate composition of black liquor for pine and birch obtained through normal pulping conditions. Kraft black liquor from birch and pine has a composition of 25-33% lignin (and mostly high molecular weight lignin), ~30% aliphatic carboxylic acids (degradation products from polysaccharides), ~10% other organics and about 30% inorganics (Niemelä and Alén 1999).

Table 4 - Typical composition of the dry matter of pine and birch kraft black liquor in percent (Niemelä and Alén 1999)

Component	**Pine, %**	**Birch, %**
Lignin	31	25
HMW (>500 Da) fraction	28	22
LMW (<500 Da) fraction	3	3
Aliphatic carboxylic acids	29	31
Formic acids	6	4
Acetic acids	4	8
Hydroxy monoacids	16	17
Hydroxy diacids	3	2
Other organics	7	11
Extractives	4	3
Polysaccharides	2	7
Miscellaneous	1	1
Inorganics	33	33
Sodium bound to organics	11	11
Inorganic compounds	22	22

2.3 Characteristic properties of technical lignins

Technical lignin is the dissolved lignin isolated from spent cooking liquor and there are several types which mostly are named after pulping method used. There are four important factors that influence the properties of the precipitated lignin; raw material i.e. type of wood, methods used to dissolve the lignin i.e. pulping process, methods used to purify the lignin, nature of chemical modification after isolation. There exist various different methods to remove lignin from wood some analytical and some more industrial with more or less commercial application. Among the industrial methods are sulphite (producing lignosulfonate lignin) and alkaline pulping (kraft, soda or soda-anthraquinone lignin), and organosolv pulping (pulping with organic solvent mixtures) just to name a few. During these separation processes the lignin undergoes significant structural changes compared to native lignin and also some of them will contain sulphur inherited from the process. The dissolved lignin will also obtain differences in properties such as solubility; where lignosulfonates are water soluble. Table 5 depicts a comparison of characteristics of lignin obtained from different pulping processes presented in a study by Mansouri and Salvado who aimed to completely characterize different technical lignins (softwood lignin) from different pulping methods, such as kraft, soda-anthraquinone, and soda, Orgoanosolv and pulping process for production of adhesives (Mansouri and Salvado 2006).

Table 5 - Results from the study by Mansouri and Salvado. The numbers in parenthesis in the kraft lignin column is the results for unpurified samples. (Mansouri and Salvado 2006)

	Kraft lignin %	**Soda-AQ lignin%**	**Organosolv lignin %**	**Lignosulfonate %**
Moisture content	3.90	2.58	7.51	5.82
Ash content	0.44 (27.10)	0.74	1.71	9.30
Total lignin	94.1	97.9	88.0	-
Klason lignin	91,3 (61,2)	86,4	92,3	-
Acid-soluble lignin	2,8 (4,9)	11,5	1,9	-
Lignosulfonate content	-	-	-	56,5
Carbohydrate	1,58 (3,28)	2,39	1,16	Not determined
Carbohydrate composition				
Glucose	0,32 (0,94)	0,29	0,36	Not determined
Xylose	1,03 (1,83)	1,80	0,46	Not determined
Arabinose	0,23 (0,51)	0,30	0,34	Not determined
Galactose	Not found	Not found	Not found	Not determined
Mannose	Not found	Not found	Not found	Not determined
OH phenolic (UV-spectroscopy)	4,50	4,40	2,66	2,00
Elemental analysis				
%C	65,00 (48,60)	65,00	63,51	44,84
%H	5,41 (4,50)	6,12	5,55	5,15
%N	0,05 (0,05)	0,17	0,02	0,02
%S	1,25 (1,68)	0,00	0,00	5,85

%O	28,24 (45,17)	28,64	30,92	44,14
Molecular weight and DP				
M_w (g/mol)	1098,7	1300,6	2800,8	Not determined
M_n (g/mol)	545,2	646,6	1123,4	Not determined
M_w/M_n	2,01	2,01	2,50	Not determined

2.3.1 Characteristics of kraft lignin

The precipitated kraft lignin will have a dark colour which arises from chromophores which are light – absorbing groups in the chemical structure. The colour limits the use of lignin but can be improved by bleaching with for example ozone, hydrogen peroxide, and chlorine dioxide (Vishtal and Kraslawski 2011). Bleaching will however alter the chemical structure. (Gellerstedt 2010c) Even though lignin in itself does not have an unpleasant odour the objectionable smells will originate from the sulphur present (mercaptans) in the process. The obtained kraft lignin is polydisperse and complex structure with various impurities such as sugars, extractives, ash, sulphur, proteins, and other compounds inherited from the raw materials and delignification process. If the impurities is not removed and the raw material homogenised it can cause formation of undesirable by-products during processing which leads to deteriorated properties in the final product. Especially sulphur acts as poison to catalysts in many chemical conversion processes. There is a large presence of organically bound sulphur and elemental sulphur, though the latter is assumed to be concentrated in the low molecular mass fractions of the dissolved lignin. (Niemelä and Alén 1999; Vishtal and Kraslawski 2011). About 70 % of the total sulphur content is chemically bonded and the rest, 30 %, can be removed by washing. The chemically bonded sulphur is difficult to remove (Svensson 2008). Helander et al. determined that the low molecular weight fraction of lignin contained a lot of chemically bound sulphur (Helander et al. 2013). Extraction process is the most widely applied method but has however little to no effect on removing sugars bonded to lignin, so called LCC-structures. Enzymatic hydrolysis followed by acid hydrolyses has been successfully tested to remove sugars from the lignin structure (Vishtal and Kraslawski 2011).

The previously described delignification reactions degrade the native lignin to fragments of both low molecular mass (monomeric and dimeric) and high molecular mass (polymeric). It is then not surprising that kraft lignin has a broad molecular mass distribution and high polydispersity (Niemelä and Alén 1999). Marton and Marton showed that hardwood kraft lignin is more polydisperse than the corresponding softwood kraft lignin (Marton and Marton 1964). However the low molecular mass fractions have lower polydispersity than the high molecular mass fraction (Niemelä and Alén 1999). In a study by Pakkanen and Alén, who investigated the molecular mass distribution from alkaline pulping of hardwood, softwood and wheat straw, it was seen that the highest molecular mass of lignin fragments decreases after H – factor 400 for hardwood and after H – factor 1200 for softwood (Pakkanen and Alén, 2012). Molecular weight of kraft lignin obtained from black liquor varies between 200 up to 200 000 grams per mole (Yoshida et al. 1987; Niemelä and Alén 1999).

Kraft lignin will inherit it structure from the dissolved lignin structure and will vary considerably with regard to original raw material (softwood or hardwood), composition, size, the presence of functional groups and the degree of crosslinking (Niemelä and Alén 1999 and Chakar and Ragauskas 2004). The extensive cleavage of β – aryl bonds during cooking leads to an increasing amount of phenolic hydroxyl groups (Gellerstedt 2010a). The oxidative cooking conditions lead to formation of quinone and catechol structures and formation of carboxyl groups. The amount of carboxylic groups decreases with molecular mass of the lignin fraction and is thereby more common in the low molecular weight lignin fractions compared to the high molecular weight fractions. The amount of condensed structures and biphenyl and biphenyl ether

structures increases towards the end of the cook and becomes more common (Niemelä and Alén 1999 and Chakar and Ragauskas 2004). The monomeric and dimeric compounds consists mostly of monolignols and substituted phenols and exhibits more structural differences compared to the polymeric fraction. There are several major types of functional groups present in the kraft lignin: hydroxyl, methoxyl, carbonyl, and carboxyl. While softwood contain exclusively (about 95%) of guaiacyl compounds, hardwood contains guaiacyl and syringyl compounds and thereby a more heterogeneous composition. Both types also contain some minor amounts of phenylpropanoid units such as catechols, methoxycatechols or pyrogallol derivatives. Eucalyptus and many other hardwoods contains has substantial amounts of polyphenolic extractives which decomposition products are identical or similar with those derived from lignin (Niemelä and Alén 1999; Vishtal and Kraslawski 2011). The heterogeneous structure and mixture of functional groups leads to unexpected behaviour and reactivity of the kraft lignin structure is limited due to few orto and para reactive sites and poor accessibility due to the complex structure. This can however be improved through structural uniformity by controlled degradation – chemical or enzymatic (Vishtal and Kraslawski 2011).

The molecular weight and structure of the lignin are important parameters in thermal properties of lignin such as the decomposition temperature and glass transition temperature. Lignin decomposes slowly over a broad temperature compared to hemicelluloses and cellulose, because various oxygen functional groups in its structure have different thermal stability. Type of raw material result in different degradation rates for lignin - as well as for the early stages of hemicellulose degradation – and softwood lignin is more stable than hardwood lignin. Decomposition of the polymer structures starts at 200 - 275^{o}C. The main decomposition process occurs around 400^{o}C with the formation aromatic compounds such as phenolics, hydroxyphenolics and guaiacyl/syringyl type of compounds. The distribution of the amount of syringyl compounds and guaiacyl compounds is of course dependent on species since softwood mainly gives guaiacyl and hardwood a mixture of guaiacyl and syringyl (Brebu and Vasile 2009). Lignin is considered as an amorphous solids with a glass transition temperature between 120^{o}C and 140^{o}C. The glass transition temperature is dependent on the structure and the molecular weight distribution regardless of plant origin or method of isolation. A high degree of aromatic contribution and substitutions as well as the molecular weight will correspond to an increase of the glass transition temperature. Both the thermal stability and the glass transition temperature increases with increasing molecular weight (Yoshida et al. 1987; Gandini and Belgacem 2008).

2.4 Isolation of lignin from black liquor

2.4.1 Precipitation of lignin from black liquor

Isolation of kraft lignin from black liquor is usually done by acidification. By first lowering the pH to 9 – 10 the lignin associates into particles and the water solubility decreases as the phenols and carboxylic acids in the lignin is protononized and thereby becoming uncharged and about 80% of dissolved lignin is precipitated as a sodium salt. Thus the precipitate will contain a lot of sodium ions and a high ash content (up to 30%) and consequently effective washing is crucial (Gellerstedt 2010b and Vishtal; Kraslawski 2011). Washing is done in lab scale by suspending the lignin in water and adding more sulphuric acid until pH 3-2 is reached as a second acidification step (Vishtal and Kraslawski 2011; Lin and Dence 1992). Hemicelluloses, and especially xylan which survive the peeling reaction in the cook and there by maintain a high molecular weight, are mostly comprised of random coils that can link the dissolved lignin macromolecules. However, the presence of hemicelluloses does not greatly influence the precipitation process but will affect the purity of the obtained lignin and the filtration properties especially for hardwood black liquor. (Wallmo et al. 2008) Temperature is an important factor during precipitation. Higher temperatures lead to larger lignin particles/agglomerates which poses problems for ultrafiltration. (Helander et al. 2013) The pH can also be lowered by using carbon dioxide gas (Bajpai. 2012). Another way to precipitate lignin is by increasing the

ionic strength by adding a multivalient cation (e.g calcium) (Sundin 2000). Table 6 depicts the fractional precipitation at different pH of kraft lignin from spruce black liquor by successive acidification with sulphuric acid from which it can be concluded that the bulk (about 70 – 85 %) of the lignin precipitates at pH 9 – 10. (Gellerstedt 2010b)

Table 6 - Fractional precipitation at different pH of kraft lignin from spruce black liquor by successive acidification with sulphuric acid (Gellerstedt 2010b)

Precipitation pH	Amount (% of total)	Sulphur content (%)
10,75	27	1,2
10,5	32	2,1
10,2	10	-
10,0	7	1,4
9,9	4	-
9,5	4	-
9,4	3	1,5
8,2	2	3,9
7,8	1	-
1,5	10	6,5

2.4.2 LignoBoost and the integrated kraft biorefinery

The use of sulphuric acid is easy to handle but can however affect the sulphur balance of the mill as well as increase the sulphur content in the dissolved lignin. The use of carbon dioxide gas avoids this imbalance but results in a more complicated mixing stage. Carbon dioxide gas is the preferred and most used method worldwide today. (Gellerstedt. 2010b, Bajpai. 2012 and Vishtal and Kraslawski 2011). Much research has been performed to develop new technologies to implement recovery of lignin in existing pulp mills. There are several that show a lot of promise such as the newly developed LignoBoost process. However, such retrofit must be accompanied by full process system analysis in order to understand the full impact on the existing process and product properties. The kraft pulp mill of today has to import energy for the processes while the integrated kraft pulp mill will be able to produce its own energy as well as new product streams (biochemical and materials) to add to the core pulp production (Bajpai. 2012).

Today lignin is considered a low-value residual and burned in the recovery boiler and the combustion energy used to maintain the high temperature needed for the reactions. The goal of the recovery boiler is to obtain the sodium carbonate and sodium sulphide in melted form. Which is then dissolved into water and the solution is then causticized in the lime kiln in high temperature (Theliander 2012). Most modern mills run there recovery boilers close to the maximum capacity and there is a surplus of energy. This makes it possible to remove lignin from the black liquor and thereby minimizing the amount of dry solids in the recovery boiler. There is then the possibility to increase the throughput of black liquor as lignin is withdrawn. However the amount of lignin that may be removed from the black liquor is mainly dependent on the status of that mill´s recovery boiler and the critical level lies between 10 – 30 % lignin removed before the performance deteriorates (Bajpai. 2012).

The LignoBoost process is a new and cost-effective process to extract lignin from black liquor and is developed by STFI-Packforsk. Lignin is precipitated from black liquor by the use of carbon dioxide gas and

then washed by counter-current washing to remove ash and sodium. The final lignin produced is considered to have good properties: 65 – 70 % dry solids content, 0,1 – 0,5 % ash, 0,01 – 0,4 % sodium and a heating value of 26 GJ per ton. The bulk of the production cost is the use of commercial carbon dioxide, but it may be possible in future to take carbon dioxide form the lime kiln. However, gas cleaning will be a challenge (Bajpai. 2012). LignoBoost lignin can be used as fuel and provides opportunity for the kraft mills to us it in the lime kiln instead of fossil fuel. The lime kiln is currently the only fossil fuel demanding part in the modern kraft mill due to its need for high temperature to drive the chemical reactions there, while the rest of the mill is self-supporting on energy from the recovery boiler. It is estimated that about 4 million cubic meters oil is used in lime kilns in the world. In a three day trail in the mill Mönsterås, owned by the company Södra, fossil fuel was successfully replace by 50% with lignin, 70 - 80% of lignin most of the time up till 100 % (Energimyndigheten 2008).

3. Materials and methods

3.1 Raw material

Wet wood chips of pine and spruce and dried eucalyptus wood chips with a dryness of 91% were obtained from a Swedish pulp mill. The wet wood chips were dried in an oven at 65°C for 24 hours to a dryness of 95%. The kraft cooking was performed using wood chips with an accepted thickness of 2 to 8 mm. The wood chips were sorted manually and wood chips with residual bark or knots were rejected.

3.2 Kraft pulping performed

All kraft pulping were done at KTH in 2,5 litre steel autoclaves where 250 gram dry weight wood chips was put into each and then evacuated with vacuum pump for 30 min. The cooking liquor, called white liquor, was then added with 4:1 liquor to wood ratio and table 7 depicts the pulping conditions used and where the only big difference is the cooking time and wood used. The autoclaves with a set slightly inclined to induce mixing while rotating into an ethylene bath. For each wood type two autoclaves were used to get enough spent cooking (black) liquor, about half a litre from each, to use for precipitation. The black liquor was collected from each point and stored in a fridge until precipitation.

Table 7 - Pulping conditions

	Pine & Spruce	**Eucalyptus**
Pulping temperature	157°C	
NaSH [M]	0,26	
NaOH [M]	1,2	1,0
Sulphidity [%]	35,6	41,3
E.A [%]	19,2	16
H-factor/pulping time	1500/ 4h 18 min	500/ 1h 38 min
	1000/ 3h 17 min	300/ 59 min
	500/ 1h 38 min	150/ 30 min

3.3 Kappa number

The kappa number was determined according to ISO 302:2004(E) on the pulps with the longest pulping time. The results for each samples were reported as the average of two samples.

3.4 Precipitation of lignin from black liquor, washing and drying

Lignin was precipitated from kraft black liquor obtained after cooking. The pH for the black liquors was around 12. The black liquors were heated to a temperature of 70°C for pine and spruce and to 60°C for eucalyptus. A 20% H_2SO_4 solution was added during rapid stirring with magnet until pH 9 was obtained. The beaker with precipitated lignin was then cooled in an ice bath and then put into the fridge overnight at which the lignin colloids assembled in the bottom of the beaker thereby allowed to sediment. The beaker with acidified black liquor phase and sedimented lignin was then carefully poured through a Büchner funnel equipped with a fine filter web (20µm that withstands high pH) at which the lignin stayed on the mesh. The lignin filter cake was then re-dispersed in distilled water and pH was lowered with sulphuric acid to 2 under rapid stirring with magnet. The lignin was filtered again (20µm that withstands low pH) and collected on a glass dish to dry in a ventilated oven at 65°C, se table in appendix. (Lin and Dence 1992; Helander 2014).

3.5 Phenolic content determination with UV- vis analysis

The phenolic content in lignin using a UV-vis was determined according to the modified method proposed by Gärtner et al. 1999. 10 mg precipitated lignin sample was dissolved in 5 ml dioxan and 5 ml of 0,2 M NaOH solution (8 grams NaOH(s) in one liter of deionized water). 2 ml of dissolved lignin solution was added to two 25 ml volumetric flasks. 0,2 M NaOH solution was added up to the 25 ml mark to the first one and a phosphate buffert with pH 6 (buffert strength of 100 mM and a mixture of 6,0716 grams per liter of monosodium phosphate with 1,6088 grams per liter disodium phosphate in 500 ml of deionized water) was added to the second one. The solutions were then analysed with SHIMADZU UV – 2550 UV – vis spectrophotometer using fused quartz cuvettes. The buffer solution with pH 6 was placed in the reference holder and the 0,2 M NaOH solution was placed in the sample holder. The absorbance was measured between 400 nm and 290 nm with medium scan speed and the peaks at 300 and 350 nm were analysed. The total phenolic content was calculated according to equation 1 based on the lignin content from analytical pyrolysis, see appendix A3. (Gärtner et al. 1999) The results for each samples were reported as the average of two samples.

3.6 Ash content and total solid content in black liquor

10 ml of each black liquor samples was placed in a ceramic cup and put into an oven with a temperature of 105°Cover night. After the gravimetrically determining the dry content, the ceramic cups were placed in an oven holding a temperature of 500°C for 6 h. The results for each samples were reported as the average of two samples.

3.7 Ash content in precipitated samples

0,3 g of each precipitated lignin sample was placed into ceramic cups and then put into the ash oven at 500°C for 6 h. The weights of dried ceramic cups, weight of sample and weight after the ash oven was noted and the ash content calculated. The results for each samples were reported as the average of two samples.

3.8 Klason lignin and carbohydrate content determination

Klason lignin content and carbohydrate composition were analysed on the precipitated lignin samples, milled pulp samples and milled wood chips samples. The amount of sample was around 200 mg for pulp and wood samples and 80 mg for the precipitated lignin samples. Klason lignin was determined gravimetrically after hydrolysis with sulphuric acid at a temperature of 125^{o}C for 60 min according to SCAN-CM 71:09. The carbohydrate content was determined on the hydrolysate eluents after acid hydrolysis using a high- performance anion exchange chromatograph quipped with pulsed amperiometric detection (HPAEC-PAD) and CarboPac PA1 column (Dionex, Ca, USA) and Klason lignin as the filtrate. The results for each samples were reported as the average of two samples.

3.9 Differential scanning chromatography (DSC)

The dried precipitated lignin samples were analysed with differential scanning chromatography (DSC) in a Mettler Toledo DSC 1 STAR^{e} System. The sample was put into 40 µl aluminium standard cups and the sample

weight noted. The sample was heated form 25°C to 150 °C at a rate of 10°C/min in nitrogen gas with a flow rate of 50 ml/min. The temperature stayed at 150°C for 3 min and then dynamically cooled to 25°C and reheated to 300°C. The glass transition temperature was recorded at the midpoint temperature of the heat capacity transition of the second heating run using the Mettler software. The results for each samples were reported as the average of two samples.

3.10 Elemental analysis (CHNS/O)

Elemental analysis was performed on all precipitated lignin samples at the Latvian State Institute of Wood Chemistry, Lignin Laboratory. About 30 mg homogenized sample is packed in tin foil, weighed and placed into carousel of the automatic sample feeder and analyzed with Elementar Analysensysteme GmbH, (Germany) Vario MACRO CHNS. Oxygen was calculated according to equation 2, appendix A5. Analysis was performed on triple samples.

3.11 Analytical pyrolysis (Py-GC/MS)

Analytical pyrolysis was performed on all precipitated lignin samples at the Latvian State Institute of Wood Chemistry, Lignin Laboratory using a Frontier Lab (Japan) Micro Double-shot Pyrolyser Py-2020iD , with pyrolysis temperature of 500°C and a heating rate of 600°C/s. Directly coupled with the Shimadzu GC/MS-QP 2010 apparatus (Japan) with capillary column RTX-1701 (Restec, USA), 60 m × 0,25 mm × 0,25 µm film, with injection temperature of 250°C with El of 70 eV, and MS scan range m/z 15-350 with gas helium at the flow rate of 1 ml/min and split ratio of 1:30. The sample size loaded was between 1,0 - 2,0 mg. The oven temperature program was 1 min isothermal at 60°C, then heated 6°C/min to 270°C, and finally held at 270°C for 10 min. The identification of the relevant peaks was performed on the basis of GC/MS chromatogram using Library MS NIST 147.LI13. The relative area of the peaks was calculated using the Shimadzu software and for some corrected or integrated manually where it was needed on the basis of the GC/MS data. The relevant peaks were averaged between the double samples.

4. Results and discussion

Wood chips from eucalyptus (Urugrandis), pine and spruce were subjected to kraft pulping to three different pulping times and the lignin was precipitated from the black liquor using sulphuric acid. The precipitated lignin was analysed by different methods to obtain an understanding of the effect of the different wood species and pulping conditions on lignin characteristics, since such characteristics will decide the possible applications. All analysis were done with double sample except in the elemental analysis in which triplets were used. For readability and clarity, the result tables from which graphs, discussion and conclusions are based have been put in the appendix and only that which is relevant for the discussion included.

4.1 Preparation of lignin samples

4.1.1 Dissolution of lignin

The lignin in the wood samples was dissolved by subjecting wood chips to kraft pulping. The pulping conditions were chosen as to represent standard conditions in industrial practice, see table 7 above. Spent liquor, so-called black liquor, and delignified wood were retrieved after different pulping times. Figure 6 shows how the delignification of the wood chips proceeded with pulping time, shown as H-factor. The longest pulping time, corresponding to an H-factor of 500 for eucalyptus and an H-factor of 1500 for pine and spruce produced a pulp with kappa number of 35 for pine, 34 for spruce and 17 for eucalyptus.

4.1.2 The precipitation of lignin from black liquor

Precipitation of lignin from black liquor used a lab scale method in which sulphuric acid was used to lower the pH.

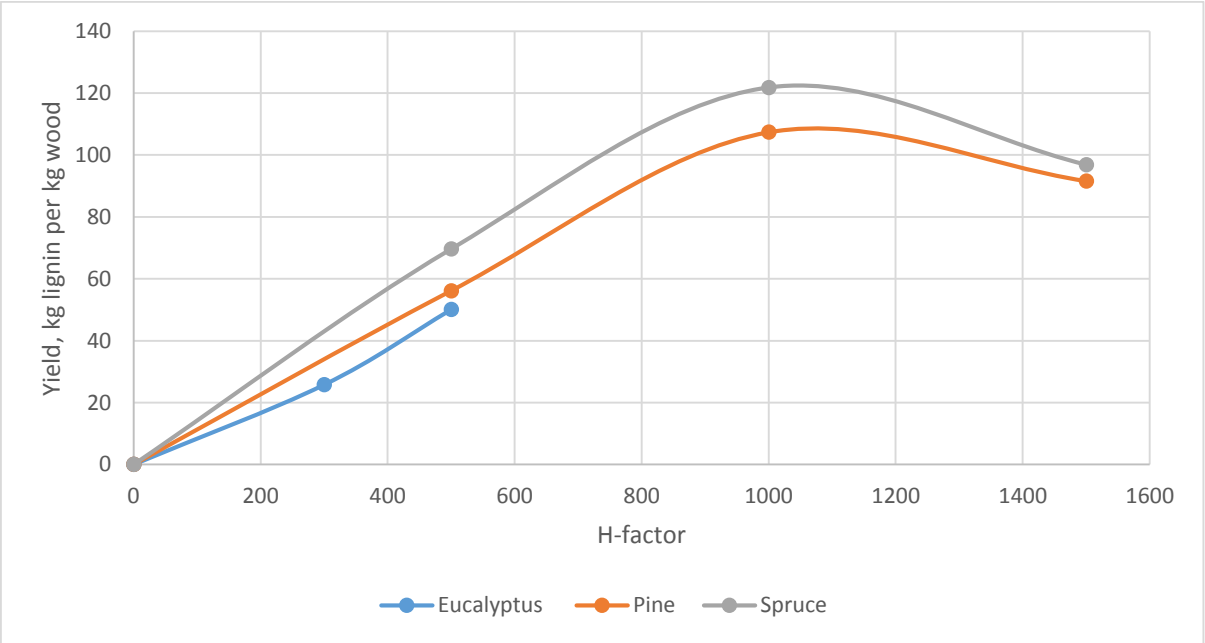

Figure 6 - Amount of precipitated lignin from black liquor at different cooking time

The decrease in Klason lignin in the wood material corresponds to an increase in dissolved lignin in the black liquor. Figure 6 depicts the amount of lignin precipitated from black liquor at the different cooking time, and the highest amount was obtained from the softwood samples. The amount of lignin precipitate from the black liquor also increased with pulping time, see figure 7 and appendix A2. This is not surprising because as the pulping progresses, the more lignin is defragmented in the wood cells and solubilized into the black liquor. It follows then intuitively that longer pulping time leads to a higher amount of lignin solubilized and available for precipitation.

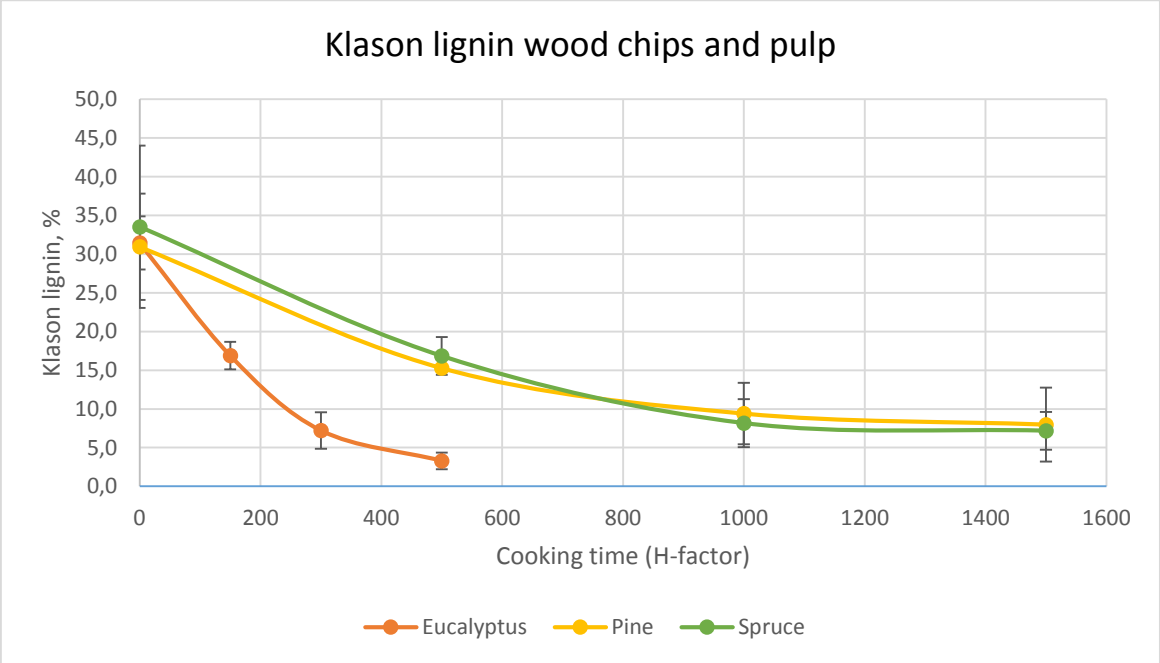

Figure 7 – Klason lignin in wood chips and pulp from different cooking times (H-factor)

It was observed that increased pulping time resulted in a more easily filtered lignin. Lignin precipitated after the longest pulping times had better flow through the filter and did not clog it. The eucalyptus lignin precipitated after the shortest pulping time however, flowed through the filter and no lignin was collected. However, according to figure 6 about half of the eucalyptus lignin in the wood is dissolved after 30 min (H-factor 150) but the associated lignin by acidification is probably not big enough to stay on the filter.

After drying in a ventilated oven at 65^{o}C it was surprising to observe the difference in colour of eucalyptus compared to spruce and pine. During washing with acidified water eucalyptus had the colour of dark coffee but after drying the colour turned greenish (maybe due to metal ions). Figure 8 depicts the colour difference.

Figure 6 - The colour of the lignin samples, from left to right; spruce, pine and eucalyptus.

4.2 Lignin characterization

The determination of Klason lignin in the precipitated samples from black liquor proved to be a bit tricky. The amount of sample used had to be considerably lower compared to the wood and pulp samples due to problems with liquor flow in the filtration step. Softwood lignin samples with the shortest cooking time (H-factors of 500 and 1000) posed the most difficulty, whereas the two eucalyptus samples and pine and spruce with longest cooking time (H-factor 1500) were easier to filter.

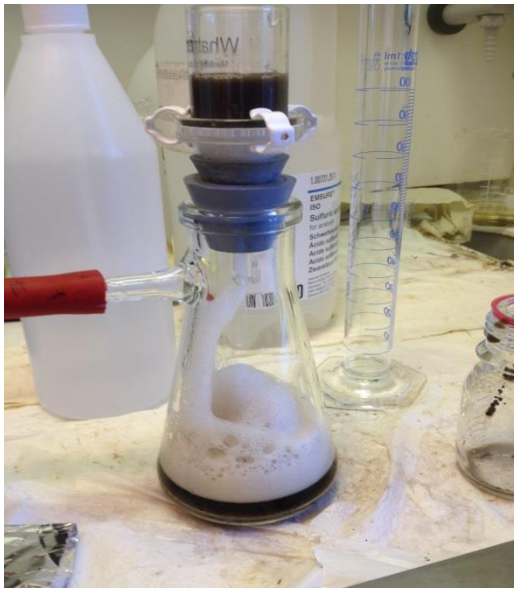

Figure 7 - Klason lignin determination on pine yielded a lot of foam indicating presence of impurities such as extractives

The softwood samples, especially pine, produced a lot of foam, as can be viewed in figure 8, indicating presence of extractives. The samples were not submitted to any extraction or purification prior to analysis meaning that the presence of foam is not entirely surprising in pine since it contains a high amount of resins (2,5 – 4,8 % in native wood) compared to other wood species; spruce (1,0 – 2,0 % in native wood). (Björklund Jansson and Nilvebrant 2010)

Figure 10 depicts the chemical composition of the black liquor precipitate with respect to lignin, ash and carbohydrates – arabinose, galactose, glucose, xylose, mannose – for eucalyptus, pine and spruce after different pulping time, determined according to acid hydrolysis and Klason lignin. The Klason lignin content in the eucalyptus samples is slightly higher than in the softwood samples. However, the higher content of lignin in the eucalyptus sample is probably caused by impurities e.g. polyphenolics present in the eucalyptus tree. The lignin samples were not subjected to any extraction prior to analysis. The Klason lignin content in

the eucalyptus black liquor precipitate may be influenced by degradation products of polyphenolics which are similar to those of lignin, which would lead to the higher amount of Klason lignin (Niemelä and Alén 1999). The ash content in the two eucalyptus samples is lower compared to the softwood samples with the two shortest cooking times (H-factor 500 and 1000 for pine and spruce). The composition in the eucalyptus samples seemed to be independent of cooking time. For the softwood samples, the amount of Klason lignin and ash varies slightly depending on cooking time. The higher content of ash in the softwood is probably due to less efficient washing. The precipitates originating from black liquor with the two shortest cooking times (H-factor 500 and 1000) were more difficult to filter compared to the softwood samples with the longest cooking time. Probably the particle size of the precipitate is different between the samples.

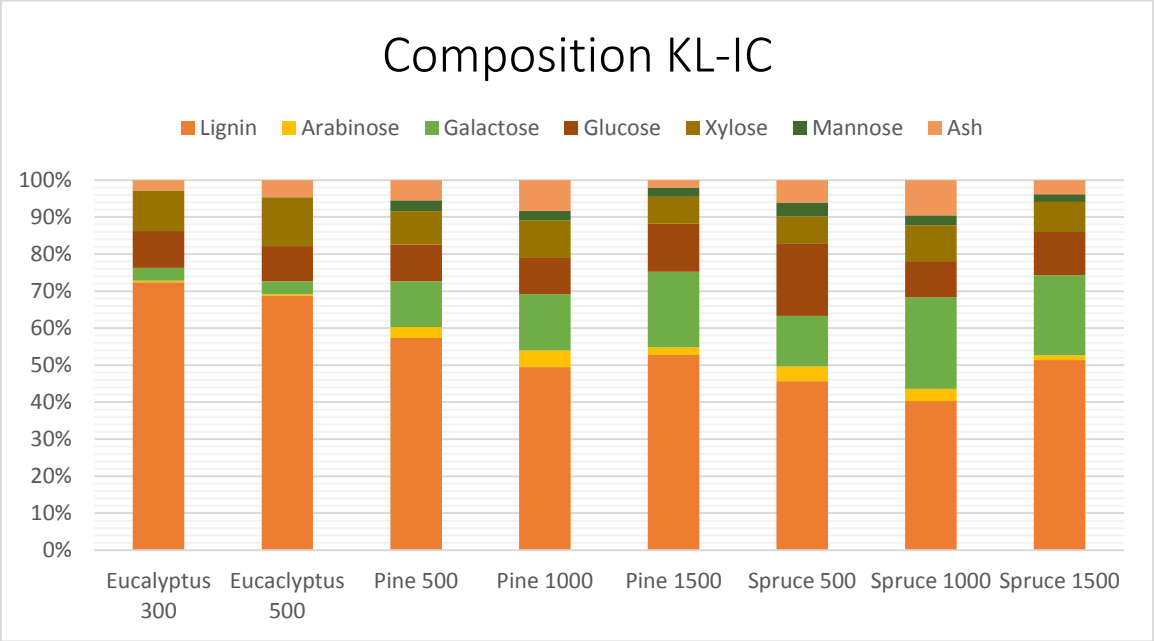

Figure 8 – Chemical composition of samples precipitated from black liquor after kraft cooking of eucalyptus, pine and spruce determined according to acid hydrolysis followed by ionic and Klason lignin. Ash content according to thermogravimetric analysis.

Figure 11 depicts the lignin and carbohydrate content obtained with the analytical pyrolysis (pyrolysis followed by gas chromatography and mass spectrophotometry, Py-GC/MS). The composition of the precipitates were independent of cooking time for all raw materials, though the amount of lignin was significantly higher (about 7%) in the softwood samples compared to eucalyptus.

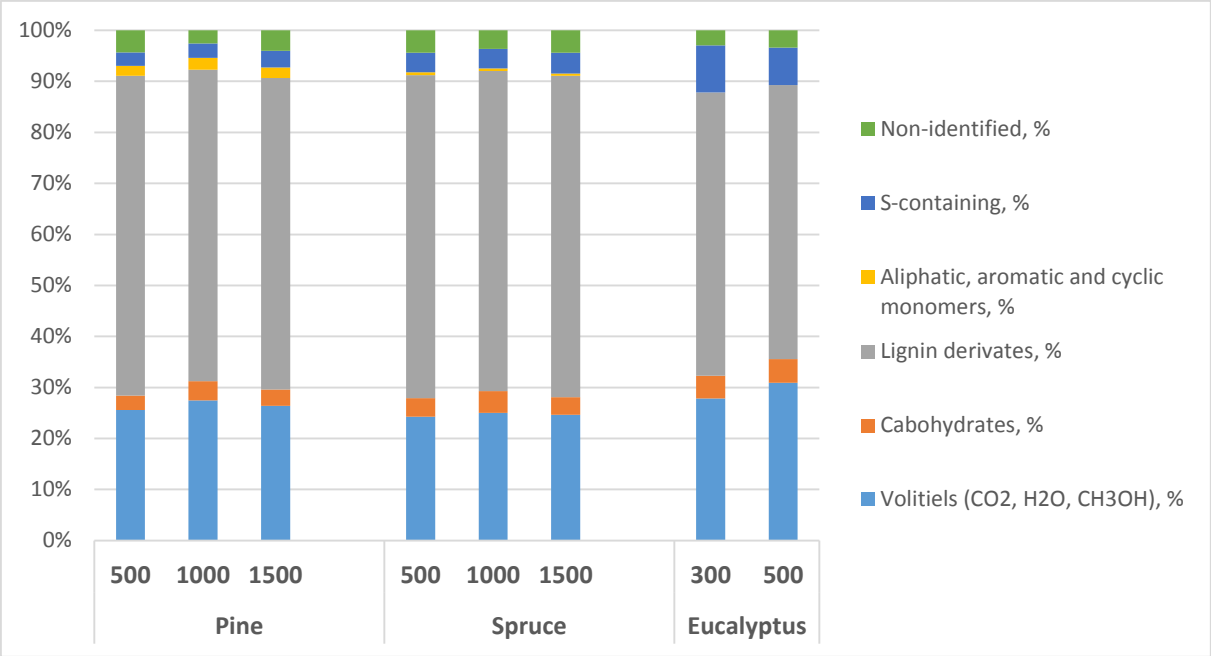

Figure 9 – Chemical composition of samples precipitated from black liquor after kraft cooking of eucalyptus, pine and spruce determined with Py-GC/MS.

El Mansour and Salvadó determined Klason lignin content in un-purified kraft lignin to be around 61% and carbohydrates around 3 %, see table 8. (El Mansouri and Salvadó 2006) The lignin and carbohydrate content determined with the Py-GC/MS, figure 11, and was consistent with the results of El Mansouri and Salvado, on their un-purified softwood kraft lignin samples. The results on lignin and carbohydrates with the KL-IC method, figure 10, were not consistent with the results by El Mansouri and Salvado, even though the precipitation method is similar. The results obtained in this study, gave a higher content of carbohydrates and in the case of the pine and spruce samples between 2-10% lower Klason lignin and in the case of eucalyptus about 10 % higher Klason lignin. The ash content in this study is much lower compared to Mansouri and Salvado which is probably due to better washing and the fact that the precipitation was done on black liquor produced in the lab.

Figure 12 depicts the variation of lignin carbohydrate ratio depending on raw material and cooking time. The lignin to carbohydrate ratio (L/C ratio) of the precipitated samples with different cooking times varied little in case of the eucalyptus and spruce but a bit more for pine. For both pine and spruce the L/C ratio was lower at the medium pulping time (H-factor 1000). This shows that the middle softwood sample, with the lowest L/C ratio, had a higher degree of contamination by carbohydrates compared to the other cooking times. This is also indicated by the results obtained from the Klason lignin content, figure 10. However, the longest and the shortest cooking times had larger quantity of lignin and less content of carbohydrates.

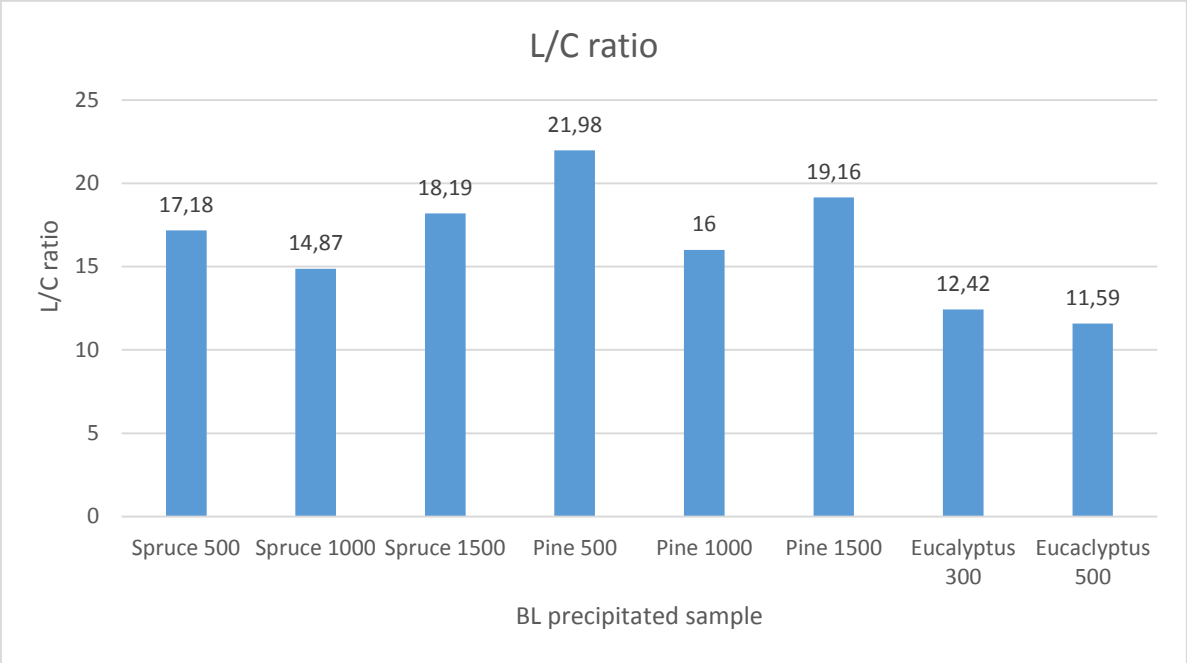

Figure 10 - Lignin carbohydrate ratio in of samples precipitated from black liquor after kraft cooking of eucalyptus, pine and spruce determined with Py-GC/MS.

Furthermore the Py-GC/MS also yielded results on the composition of the lignin, figure 13, in terms of guaiacyl, syringyl and phenyl and benzyl derivatives with results without any surprising elements. Softwood as expected to consisted mainly of guaiacyl derivates and phenyl and benzyl derivates and there was no change in the amount depending on cooking time. Nor was there any change in the composition of syringyl/guaizyl and phenyl and benzyl derivates depending on pulping time in eucalyptus lignin. Which is consistent with the Py-GC/MS results of kraft eucalyptus lignin at different kappa numbers (different amount of residual lignin, i.e. different cooking time) by Prinsen et al. (Prinsen et al. 2013).

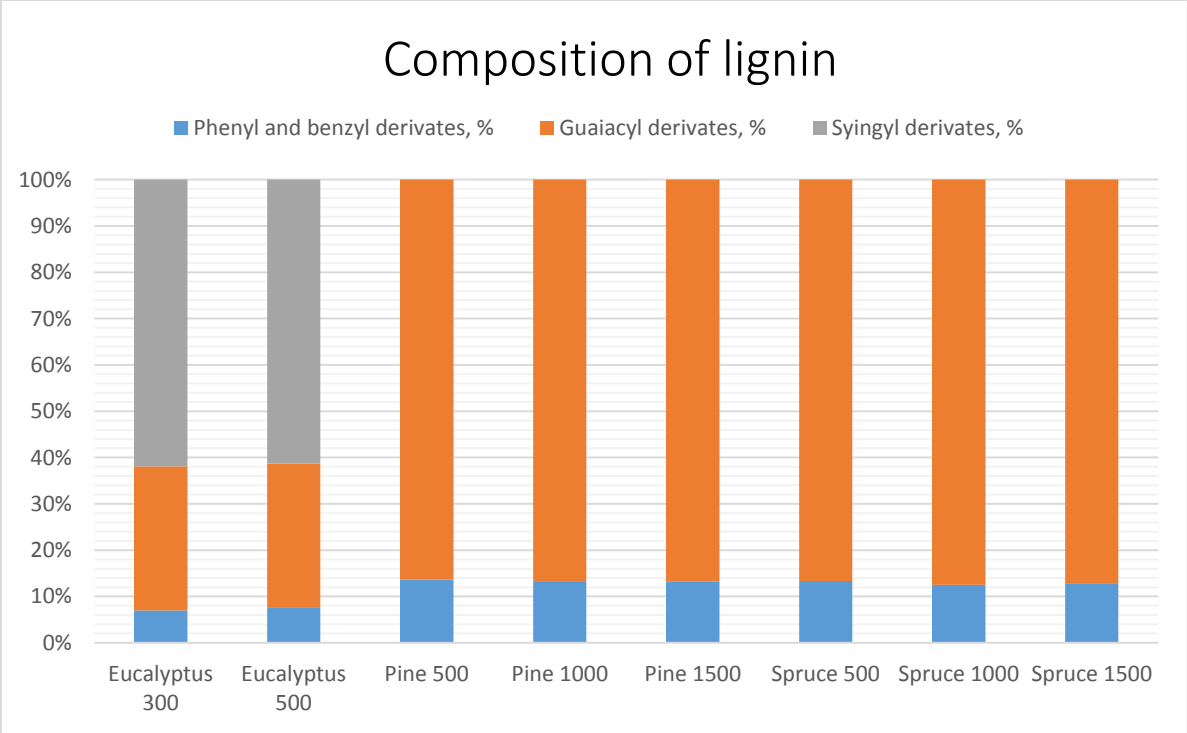

Figure 11 - Composition of lignin in precipitated samples

The results from the elemental analysis are depicted in table 8. The elemental analysis gave results of the atomic composition of nitrogen, carbon, hydrogen and sulphur and oxygen was calculated as the rest. The calculation of the amount oxygen is a good estimation since the black liquor from which the lignin is precipitated was produced in laboratory, and will thereby not be influenced of process elements as industry black liquor. Table 8 gives the amount in percent of the different atomic composition for the different raw material and cooking time. The interesting factors for possible applications are the content of sulphur, oxygen and carbon. The highest amount of sulphur from the elemental analysis is found in the eucalyptus samples. The amount of sulphur seemed to be independent of cooking time.

Table 8 - Results from the elemental analysis

Precipitated sample	N, %	C, %	H, %	S, %	O calc, %
Pine 500	0,18±0,10	62,22±0,48	5,26±0,16	2,81±0,17	29,53±0,51
Pine 1000	0,13±0,06	58,03±0,71	5,02±0,09	4,35±0,25	32,46±0,65
Pine 1500	0,27±0,05	63,14±0,77	5,31±0,40	3,16±0,42	28,28±0,64
Spruce 500	0,20±0,04	59,24±1,01	5,02±0,19	3,82±0,16	31,41±1,21
Spruce 1000	0,14±0,02	58,21±0,33	4,81±0,30	4,75±0,46	32,09±0,64
Spruce 1500	0,23±0,12	62,58±0,92	5,22±0,07	3,33±0,58	28,66±0,29
Eucalyptus 300	0,19±0,04	58,43±0,72	5,09±0,07	4,32±0,43	31,98±0,39
Eucalyptus 500	0,17±0,03	57,43±0,17	4,93±0,38	4,57±0,80	32,09±0,31

In figure 14, the sulphur content of the lignin precipitates from eucalyptus, pine and spruce determined by elemental analysis and Py-GC/MS are compared. There was no systematic difference between the two methods. In the case of eucalyptus lignin, Py-GC/MS showed a significantly higher sulphur content compared to elemental analysis, but for the softwood lignins Py-GC/MS gave both higher and lower values compared to elemental analysis. The methods gave different results on the trend depending on cooking time. According to Py-GC/MS, the sulphur content in the softwood lignins was lowest at medium cooking time, whereas according to elemental analysis there was a maxima in sulphur content at medium cooking time. Both methods, however, gave a higher sulphur content for eucalyptus than for softwood lignin. The eucalyptus samples contained a higher amount of sulphur independently of cooking time according to the elemental analysis. But the difference is more pronounced when comparing the results on sulphur content from Py-GC/MS analysis. There was a slightly higher amount of sulphur in the eucalyptus sample with the shorter cooking time.

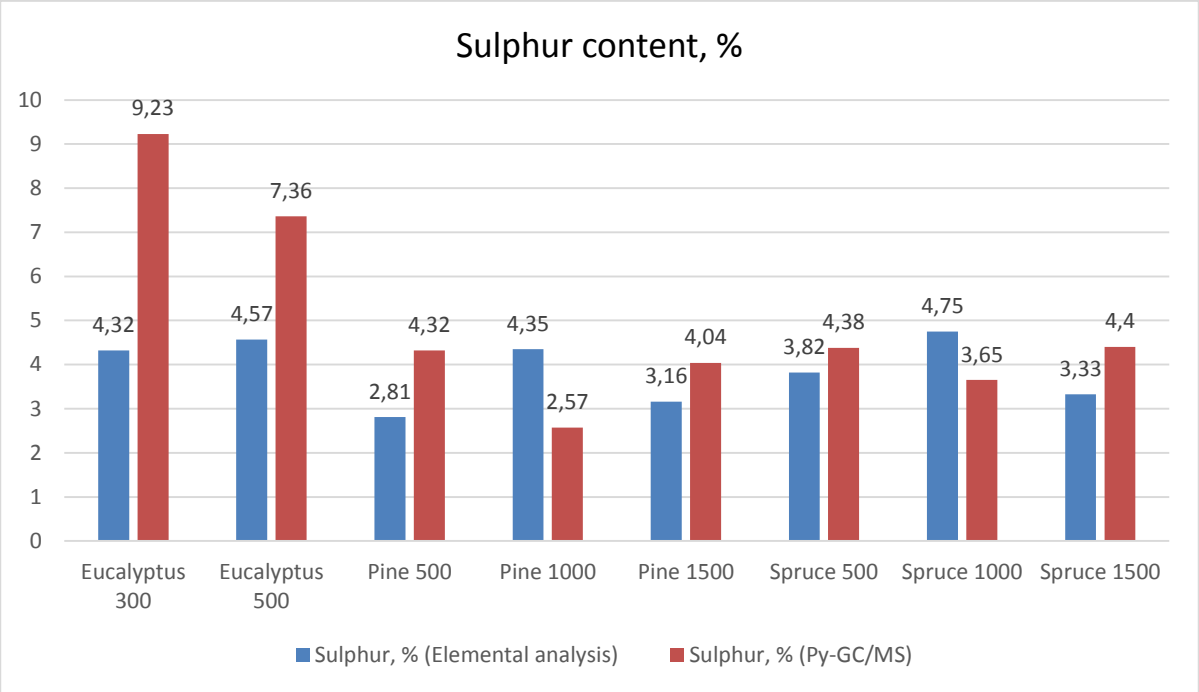

Figure 12 - Sulphur content determined by elemental analysis and Py-GC/MS

The increase of phenolic content was not surprising since the excessive cleavage of β-aryl bonds leads to an increase in phenolic hydroxyl groups. (Robert et al. 1984; Chakar and Ragauskas 2004) What is interesting is the changes with cooking time and the difference in the raw materials. Though figure 15 indicates there were some differences depending on raw material and cooking time it is currently difficult to draw any conclusions from this graph, see appendix A3. However, the phenolic content is a very important and the indications are interesting thereby more work with this method and on these samples should be done to confirm any differences.

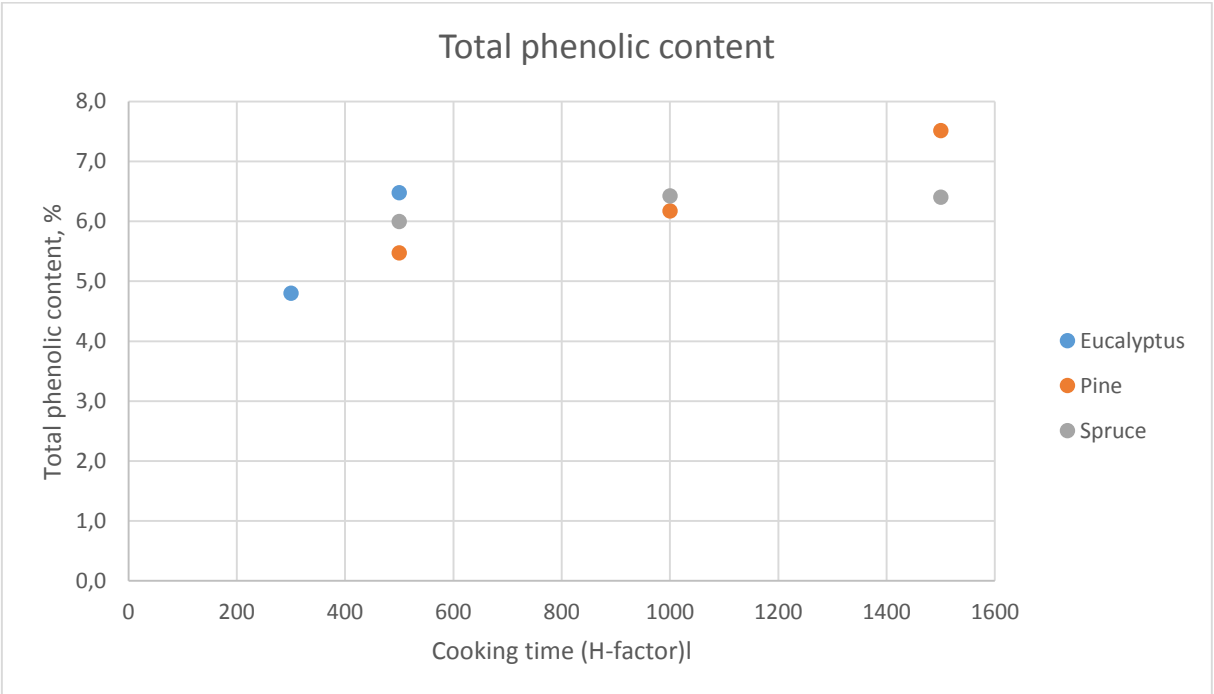

Figure 13 - Total phenolic content in eucalyptus, pine and spruce a the different H-factors (pulping time)

The glass transition temperatures were within the normal T_g range of lignin. (Gandini and Belgacem 2008) A very interesting difference between eucalyptus, pine and spruce lignin is also indicated in the glass transition temperature value (T_g), see table 11 and appendix A4. The obtained Tg values are within the normal range for lignin and similar to values obtained in previous studies. (Helander et al. 2014; Norberg 2012; Gandini and Belgacem 2008) Spruce with the longest cooking time had the highest T_g, 132^{o}C, followed by pine at 123^{o}C and then eucalyptus which has the lowest, 119^{o}C. The T_g value is however highly dependent on the aromatic composition and molecular weight of the lignin. (Gandini and Belgacem 2008; Yoshida et al. 1987). The highest T_g for spruce lignin from black liquor with the longest cooking time indicates that it probably had the highest molecular weight. One can speculate that spruce had a longer pulping time than eucalyptus so there may have been more time for condensation reactions to occur. A more condensed softwood lignin structure might explain the higher T_g compared to eucalyptus lignin. (Chakar and Ragauskas 2004) Eucalyptus had the lowest T_g value and the second highest total phenolic content. However, to draw any conclusions further analysis is needed and the most important is to determine the molecular weight of the samples fully confirm any trend. There was an indication of a trend considering the fact that the glass transition temperature is dependent on the aromatic structure (Gandini and Belgacem 2008; Yoshida et al. 1987). The softwood samples had the highest Tg and the highest phenolic content and might give the highest molecular mass compared to the eucalyptus samples with lower Tg and total phenolic content. The softwood samples has longer cooking time than the hardwood samples and thereby giving longer time for the lignin-lignin reactions. The weight molecular mass increases with the cooking time (Robert et al. 1984) and it is expected that the softwood samples will have the molecular mass.

Table 9 - Glass transition temperature for precipitated samples. The value is ± standard deviation

Sample	Glass transition temperature, ^{o}C
Eucalyptus 300	123±1
Eucalyptus 500	119±1
Spruce 500	125±0
Spruce 1000	132±1
Spruce 1500	132±0
Pine 500	116±2
Pine 1000	115±1
Pine 1500	123±2

5. Conclusions

Longer cooking time resulted in a more easily filterable lignin precipitate. Softwood lignin from kraft cooks with the longest cooking time had the highest Tg. Lignin from the kraft cook of pine with longest cooking time had the highest phenolic content.

Kraft pulping of pine resulted in higher amount of dissolved lignin, compared to spruce and eucalyptus. Eucalyptus lignin contained more sulphur than spruce and pine lignin. The relative content of lignin and carbohydrate of the lignin precipitate was similar, independent of raw material and cooking time according to the Py-GC/MS results

6. Suggestion for future work

This master thesis has examined and compared the effect of raw material, eucalyptus, pine and spruce, and cooking time on some of the physic-chemical properties of dissolved lignin. The overall goal of the project was to understand the relationship between process conditions and the structure and properties of the dissolved lignin. The question is however not yet fully investigated and there are avenues and properties to investigate.

The following would be interesting to do:

- Analyse the graph from the thermal gravimetric analysis (TGA) for the precipitated samples
- Further analysis the results of the Py-GC/MS
- Work with the UV-method for determine the phenolic content
- Re-analyse the glass transition temperature
- Size exclusion chromatography (SEC) to determine the molecular weight and polydispersity of the precipitated samples at the different cooking times
- NMR analysis to obtain more information about the structure
- Investigate the impact of the drying method by using freeze drying instead
- Analyse the amount and properties of the extractives present in the precipitated samples and their impact
- Metal analysis (ICP) on the eucalyptus samples to investigate the difference in colour
- Precipitate lignin from black liquor produced with the lab circulation digester and investigate the same properties and compare

7. References

Bajpai P., (2012). *Biotechnology for Pulp and paper Processing, chapter 19, Integrated Forest Biorefinery.*

DOI 10.1007/978-1-4614-1409-4_19, Springer Scienc + Business media, LLC. Page. 375-402

Björklund Jansson, M., Nilvebrant, N-O., (2010). *The Ljungberg textbook Biofiber Chemistry: chapter 7, Wood extractives.* Fiber and Polymer Technology, KTH, Sweden. Page. 134 -158

Brebu, M., Vasile, C., (2010). *Thermal degradation of lignin – a review.* Cellulose Chemistry and Technology, 44 (9), 353-363

Cazacu G., Capraru M., Popa V. I**.,** (2013). *Advances in Natural Polymers: Their blends, composites and nanocomposites, Volume 18, chapter 8, Advances concerning lignin utilization in new materials.* Springer-Verlag Berlin Heidelberg. Page. 255- 312

Chakar F. S., Ragauskas A. J., (2004). *Review of current and future softwood kraft lignin process chemistry.* Industrial Crops and Products 20, 131-141

Daniel G. (2010). *The Ljungberg textbook Biofiber Chemistry, chapter 3, Wood and Fiber Morphology*. Fiber and Polymer Technology, KTH, Sweden. Page. 33 -56

El Mansouri, N-E., Salvadó, J., (2006). *Structural characterization of technical lignins for the production of adhesives: Applcation to lignosulfonate, kraft, soda-anthraquinone, organolsov, and ethanol process lignins.* Industrial Crops and Products (24), 8-16

Enegimyndigenten Pressmedelenade, 26 may 2008. Available at: www.energimyndigheten.se/Global/Forskning/Nyheter/Pressmedelande%20slutgiltig%20version_sv-pdf

Downloaded: 2014-01-23

Gandini, A., Belgacem, M. N., (2008). *Monomers, Polymers and Composites from renewable resources, chapter 11, lignin as components of macromolecular materials.* Elsevier, page. 243-271

Gellerstedt G. (2010)a. *The Ljungberg textbook Biofiber Chemistry: chapter 20, Chemistry of Chemical Pulping.* Fiber and Polymer Technology, KTH, Sweden. Page. 273 -301

Gellerstedt G. (2010)b. *The Ljungberg textbook Biofiber Chemistry: chapter 55, Products and chemicals from wood.* Fiber and Polymer Technology, KTH, Sweden. Page. 363-381

Gellerstedt G. (2010)c. *The Ljungberg textbook Biofiber Chemistry: chapter 26, Chemistry of bleaching pulps.* Fiber and Polymer Technology, KTH, Sweden. Page. 325-361

Gärtner, A., Gellerstedt, G., Tamminen, T., (1999). *Determination of phenolic hydroxyl groups in residual lignin using a modified UV-method.* Nordic Pulp and Paper Research Journal, 14(2), 163-170

Helander, M., Theilander, H., Lawoko, M., Henriksson, G., Zhang, L., Lindström, M. E., (2013)A. *Fractiontion of Technical Lignin: Molecular Mass and pH Effects.* Bioresources 8(2),2270-2282

Helander, M., Sevastyanova, O., Chowdhury, S., Lange, H., Zhang, L., Wedin, H., Crestini, C., Ek, M., Kadla, J. F., Lindström, M. E., (2013)B. *Evaluation of physic-chemical properties and and prediction of spinning parameters for high quality lignins produced by ultrafiltration of industrial kraft pulping liquor.* Doctoral Thesis In Fiber and Polymer Science. Paper III. Royal Institute of Technology. School of Chemical Science and Engineering. Stockholm, Sweden 2014.

Henriksson G. (2010). *The Ljungberg textbook Biofiber Chemistry, chapter 6, Lignin*. Fiber and Polymer Technology, KTH, Sweden. Page. 109 -132

Lawoko, M., Henriksson, G., Gellerstedt, G,. (2005). *Structural differences between the lignin – carbohydrate complexes present in wood and in chemical pulps.* Biomacromolecules, 6, 3467-3473

Lin, S. Y., Dence, C. W., (1992). *Methods in lignin chemistry.* Springer-Verlag berlin Heidelberg.

Marton J., Marton T., (1964). *Molecular weight of kraft lignin.* Tappi, 47 (8), 471-476

Niemelä, K. Alén, R. (1999). *Analytical Methods in Wood Chemistry, Pulp and Papermaking: Characterization pf pulping liquor.* Editors: Sjöström, E. and Alén, R. Springer, Berlin, 316 pp. 193-232

Nordberg, I. (2012). *Carbon fibres from kraft lignin.* Doctoral Thesis. Royal Institute of Technology. School of Chemical Science and Engineering. Department of Pulp and Paper Chemistry and Technology

Pakkanen, H., Alén, R., (2012). *Molecular mass Distribution of Lignin from Alkaline Pulping of Hardwood, Softwood and Wheat Starw.* Journal of Wood Chemistry and Technology, 32, 279-293

Prinsen, P., Rencoret, J., Gutiérrez, A., Liitja, T., Tamminen, T., Colodette, J. L., Berbis, M. A., Jiménez-Barbero, J., Martínez, A. T., del Rio, J. C., (2013). *Modificaion of the Lignin Structure during Alkaline Delignification of Eucalyptus Wood by Kraft, Soda-AQ, and Soda-O_2 Cooking.* Industrial & Engineering Chemistry Research, 52, 15702-15712

Robert, D. R., Gellerstedt, G., Lindfors, E. L., (1984). *Sructural changes in lignin during kraft cooking, Part 3. On the structure of dissolved lignins.* Journal of Wood Chemistry and Technology, 4(3), 239-263

Santos R. B., Hart P. W., Jameel H., Chang H. (2013). *Wood based lignin reactions important to the biorefinery and pulp and paper industries*. BioResources 8 (1), 1456-1477

Sjöström E. (1993). *Wood Chemistry: Fundamentals and Applications*. Academic Press. ISBN 0-12-647480-X.

Sundin, J., (2000). *Precipitation of kraft lignin under alkaline conditions.* Doctoral Thesis. Royal Institute of Technology. School of Chemical Science and Engineering. Department of Pulp and Paper Chemistry and Technology

Svensson, S. (2008). *Minimizing sulphur content in kraft lignin.* Degree project. Märlardalen University. 35p. Available via: http://www.diva-portal.org/smash/get/diva2:1676/FULLTEXT01.pdf

Theliander H. (2012). *The Ljungberg textbook Chemistry of a Biorefinery, Chapter 29, Recovery of cooking chemicals: the treatment and burning of black liquor.* Fiber and Polymer Technology, KTH, Sweden. Sid. 175 -214

Vishtal, A., Kraslawski, A., (2011). *Challenges in Industrial Applications of Technical Lignins.* Bioresourses, 6(3), 3547-3568

Wallmo, H., Theliander, H., Jönsson, A.-S., Wallberg, O., Lindgren, K. (2008). *The influence of hemicelluloses during the precipitation of lignin in kraft liquor.* Wallmo, H. Doctorial thesis paper 3. Chalmers University of Technology. Department of Chemical and Biological Engineering

Yoshida, H., Mörck, R., Kringstad, K. P., (1987). *Fractionation of Kraft Lignin by Successive Extraction with Organic Solvents.* Holzforschung 41(3), 171-176

Appendix

Here is presented all results obtained in this study from which the discussion and conclusions are based. However, it does not present the numbers for the doublets (or triplets as is the case for the elemental analysis) but only the average.

A1. Composition data on wood, pulp and lignin

All data in this chapter are labeled: type/ raw material/ H-factor

LE	Lignin eucalyptus
LP	Lignin pine
LS	Lignin spruce
PE	Pulp eucalyptus
PP	Pulp pine
PS	Pulp spruce
WE	Wood chips eucalyptus
WP	Wood chips pine
WS	Wood chips spruce

Table 10 - Composition of precipitated lignin samples at the different H-factors.

Sample	Ash%	Lignin%	Arab%	Gala%	Glu%	Xyl%	Man%
LE300	3	72	0,4	3,4	9,9	11,0	0,0

LE500	5	71	0,4	3,5	9,8	13,6	0,1
LP500	7	70	3,7	15,1	12,1	11,0	3,6
LP1000	10	58	5,3	17,9	11,5	11,9	3,0
LP1500	2	57	2,2	22,1	14,0	7,8	2,7
LS500	6	48	4,2	14,5	20,8	7,7	3,9
LS1000	10	43	3,4	26,3	10,4	10,3	2,9
LS1500	4	51	1,3	21,2	11,5	8,0	2,0

Table 11 - Composition of wood chips and pulp at the different H-factors

Sample	**KL %**	**Arab%**	**Gala%**	**Glu%**	**Xyl%**	**Man%**
WE	31,4	0,1	1,1	56,4	10,0	1,0
PE150	16,9	0	0,7	76,2	6,1	0,1
PE300	7,2	0	0,4	86,0	5,3	1,2
PE500	3,3	0	0,1	88,7	7,9	0,0
WS	33,5	0,5	1,9	49,1	2,3	12,6
PS500	6,8	0,4	0,6	71,6	2,8	7,8
PS1000	8,2	0,3	0,3	80,	3,0	8,1
PS1500	7,0	0,7	0,7	79,3	3,1	9,0
WP	30,9	0,7	1,6	51,1	1,6	14,1
PP500	15,3	0,3	0,3	74,2	2,7	7,3
PP1000	9,4	0,4	0,4	79,4	2,0	8,4
PP1500	8,0	0,4	0,4	80,7	2,2	8,3

A2. Yield calculations

Table 12 - Kappa number of pulp and Black Liquor (BL) total solid content (TSC) and ash content on TSC BL

Sample	**Kappa number pulp**	**BL Total solid content, %**	**BL ash content on TSC, %**
Eucalyptus 150		11	**7**
Eucalyptus 300		13	9
Eucalyptus 500	17	14	10
Pine 500		16	10
Pine 1000		16	10

Pine 1500	35	17	11
Spruce 500		15	9
Spruce 1000		16	11
Spruce 1500	34	17	11

Table 13 - Liter Black Liquor used to precipitate lignin and amount precipitate obtained after washing and drying

Sample	**BL used (liter)**	**Precipitate, (gram/500 gram dry wood chips)**
Eucalyptus 300	1	11,6
Eucalyptus 500	1	23,3
Pine 500	1	22,4
Pine 1000	1	19,4 (44)
Pine 1500	1	37,5
Spruce 500	1	27,5
Spruce 1000	0,8	38,8
Spruce 1500	0,9	34,6

A3. UV Phenolic content results and calculations

Table 14 - Measured absorption at 300 nm and 350 nm, concentration and determined phenolic content

Sample	**Weight sample, g**	**Abs 300 nm**	**Abs 350 nm**	**Phenolic content, %**
Euc 300	0,101	0,46506	0,49561	4,8±12,8

	0,105	0,3061	0,40126	
Euc 500	0,102	0,56601	0,58421	6,5±2,02
	0,104	0,57625	0,54066	
Pine 500	0,099	0,48988	0,54843	5,5±0,89
	0,103	0,52235	0,56535	
Pine 1000	0,103	0,57637	0,5536	6,2±3,39
	0,102	0,62292	0,57664	
Pine 1500	0,102	0,65709	0,61766	7,5±8,84
	0,101	0,80879	0,65205	
Spruce 500	0,1	0,56725	0,69936	6,0±5,61
	0,1	0,48712	0,60893	
Spruce 1000	0,098	0,5793	0,59511	6,4±0,97
	0,101	0,62573	0,5591	
Spruce 1500	0,1	0,63821	0,61664	6,4±4,15
	0,101	0,58543	0,57338	

Equation 1 - Total phenolic content

$$Total\ phenolic\ content = \left((0{,}250 \times A_{300\ nm} + 0{,}107 \times A_{350\ nm})\frac{1}{l \times c}\right)\left[\frac{mmol}{g}\right] \quad [1]$$

$A_{300\ nm} = Absorbance\ at\ 300\ nm$

$A_{350\ nm} = Absorbance\ at\ 350\ nm$

$c = concentration\ of\ solution\ in\ UV - vis$

$l = lenght\ of\ fused\ quartz\ cuvettes$

A4. Differential scanning chromatography results

Table 15 - Glass transition temperature in Celsius of the precipitated samples

Sample	**Glass transition temperature, ^{o}C**
Eucalyptus 300	123±7
Eucalyptus 500	119±8
Spruce 500	125±1
Spruce 1000	132±10
Spruce 1500	132±2
Pine 500	116±17
Pine 1000	115±1
Pine 1500	123±18

A5. Elemental analysis results

Table 16 - Elemental analysis results of nitrogen, carbon, hydrogen and sulfur for the different precipitated lignin samples and the amount of oxygen calculated with equation 2.

Precipitated sample	**N, %**	**C, %**	**H, %**	**S, %**	**O calc, %**
Pine 500	0,18±0,10	62,22±0,48	5,26±0,16	2,81±0,17	29,53±0,51
Pine 1000	0,13±0,06	58,03±0,71	5,02±0,09	4,35±0,25	32,46±0,65
Pine 1500	0,27±0,05	63,14±0,77	5,31±0,40	3,16±0,42	28,28±0,64
Spruce 500	0,20±0,04	59,24±1,01	5,02±0,19	3,82±0,16	31,41±1,21
Spruce 1000	0,14±0,02	58,21±0,33	4,81±0,30	4,75±0,46	32,09±0,64
Spruce 1500	0,23±0,12	62,58±0,92	5,22±0,07	3,33±0,58	28,66±0,29
Eucalyptus 300	0,19±0,04	58,43±0,72	5,09±0,07	4,32±0,43	31,98±0,39
Eucalyptus 500	0,17±0,03	57,43±0,17	4,93±0,38	4,57±0,80	32,09±0,31

Equation 2 - Percent oxygen from elemental analysis

$$Oxygen\,\% = 100\,\% - N\,\% - C\,\% - S\,\% - H\% \qquad [2]$$

A6. Analytical pyrolysis results

Table 17 - Results from Py-GC/MS

	Spruce			Pine			Eucalyptus	
	500	**1000**	**1500**	**500**	**1000**	**1500**	**300**	**500**
	%	**%**	**%**	**%**	**%**	**%**	**%**	**%**
Carbohydrates (C)	3,68	4,22	3,46	2,85	3,81	3,19	4,47	4,63
Lignin derivates (L)	63,28	62,78	62,99	62,66	61,00	61,06	55,54	53,71
Summary C+L = 100%	66,96	67,00	66,45	65,51	64,81	64,25	60,01	58,34
Carbohydrates, % from C+L	5,50	6,30	5,21	4,35	5,88	4,96	7,45	7,94
Lignin derivates, % from C+L	94,50	93,70	94,79	95,65	94,12	95,04	92,55	92,06
C/L	0,0582	0,0672	0,055	0,0455	0,0625	0,0522	0,0805	0,0862
L/C	17,1818	14,873	18,1939	21,9885	16,0068	19,1613	12,4228	11,5945
Carbohydrates (% from chromatogram)	3,68	4,22	3,46	2,85	3,81	3,19	4,47	4,63
Acid, Ester	0,58	0,78	0,70	0,59	0,81	0,63	0,89	0,99
Aldehyde, Ketone	1,13	1,49	1,09	0,81	1,21	0,88	0,27	0,27
Cyclopentane derivates	0,62	0,69	0,63	0,53	0,74	0,64	0,22	0,24
Furan	1,01	0,82	0,66	0,73	0,77	0,74	3,01	3,05
Pyran	0,09	0,18	0,13	0,06	0,11	0,13	0,08	0,08
Sugars	0,25	0,26	0,25	0,13	0,17	0,17		
Carbohydrates, 100%	**% from total C**							
Acid, Ester	15,76	18,48	20,23	20,70	21,26	19,75	19,91	21,38
Aldehyde, ketone	30,71	35,31	31,49	28,70	31,76	27,59	6,04	5,83
Cyclopentane derivates	16,85	16,35	18,21	18,60	19,42	20,06	4,92	5,18
Furan	27,4	19,43	19,08	25,61	20,21	23,20	67,34	65,87
Pyran	2,54	4,27	3,76	2,11	2,89	4,08	1,79	1,74
Sugars	6,87	6,16	7,23	4,56	4,46	5,32		
Lignin derivatives, (% from chromatogram)	63,28	62,78	62,99	62,66	61,00	61,06	55,54	53,71
Phenyl and benzyl derivates	8,47	7,87	8,00	8,59	8,02	8,10	3,88	4,05
Guaiacyl derivates	54,81	54,91	54,99	54,07	52,98	52,96	17,27	16,74
Syringyl derivates							34,39	32,92

Lignin drivates, 100 %	**% from total L**							
Phenyl and benzyl derivates	13,38	12,54	12,70	13,71	13,15	13,27	6,99	7,54
Guaiacyl derivates	86,62	87,46	87,30	86,29	86,85	86,73	31,09	31,17
Syringyl derivates							61,92	61,29
Identified (from chromatogram)	95,62	96,35	95,60	95,68	97,43	95,96	97,06	96,62
Summary: CO2, H2O, CH3OH	24,25	25,04	24,65	25,56	27,45	26,39	27,82	30,92
Carbohydrates	3,68	4,22	,46	2,85	3,81	3,19	4,47	4,63
Lignin derivates	63,28	62,78	62,99	62,66	61,00	61,06	55,54	53,71
Aliphatic, aromatic and cyclic monomers	0,56	0,47	0,46	1,99	2,37	2,09		
S-containing	3,85	3,84	4,04	2,62	2,80	3,23	9,23	7,36
Non identified (from chromatogram)	4,38	3,65	4,40	4,23	2,57	4,04	2,94	3,38